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MEMORANDUM FOR PRS (In-House Contractor Publication)

FROM: PROI (STINFO) 08 May 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-101**
Tim Haddad (ERC) and Brent Viers (PRSM), "Organic Polymers Modified with Inorganic Polyhedra"

Canadian Society for Chemistry **(Statement A)**
(2-5 June 2002, Vancouver, Canada) **<u>(Deadline: 31 May 2002)</u>**

ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA.

Timothy S. Haddad and Brent D. Viers
ERC Inc., Air Force Research Lab,
10 E Saturn Boulevard
Edwards Air Force Base, CA 93524

Nanostructured composites of thermoplastics and inorganic clusters have been developed by incorporating polyhedral oligomeric silsesquioxane (POSS) macromers into organic polymers. These hybrid inorganic/organic thermoplastics based on styrenes, acrylics, imides, norbornenes or siloxanes, are reinforced by covalently linking monodisperse inorganic POSS clusters to the polymer backbone. A typical POSS-macromer, $R_7P(Si_8O_{12})$, is a well-defined octomeric polyhedron containing a single "P" functionality for polymerization and seven "R" groups to solubilize and compatibilize the inorganic filler with the organic matrix. A nanoreinforcement effect from the POSS groups is strongly influenced by the seven "R" groups (cyclopentyl, cyclohexyl, isobutyl or phenyl). Covalently attached POSS groups result in significant change to the observed characteristic relaxation time of the polymer; rheological measurements on molten polymer indicate that interactions between the POSS groups generate a reversible network material with rubbery properties. TEM images show that the inorganic POSS moieties associate to form a nanoscale network within the polymer matrix.

ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA

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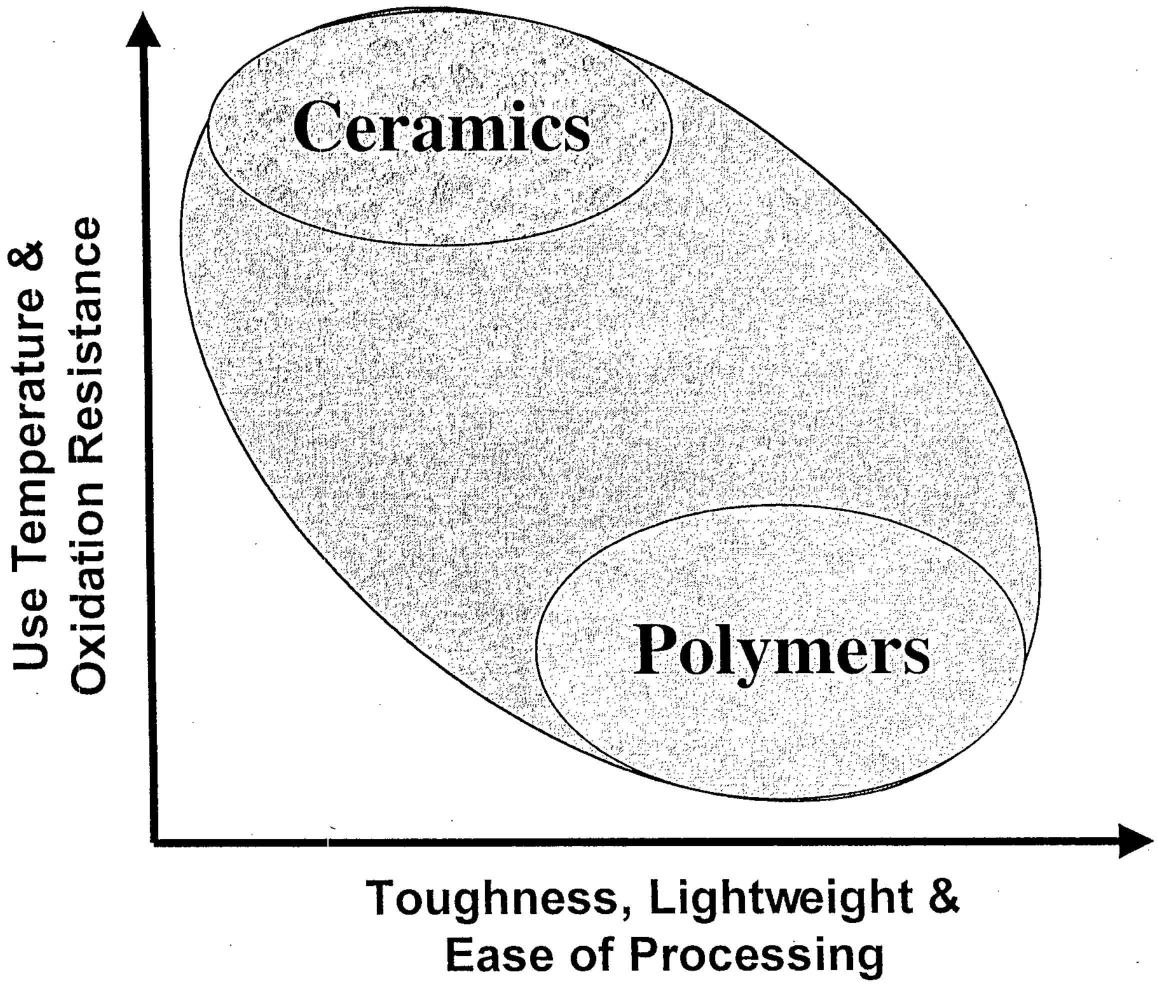
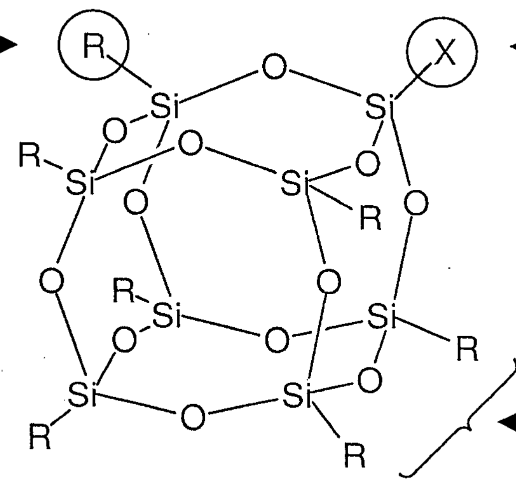
Hybrid Inorganic/Organic Polymers



- Hybrid plastics can bridge the differences between ceramics and polymers

Anatomy of a POSS Macromer

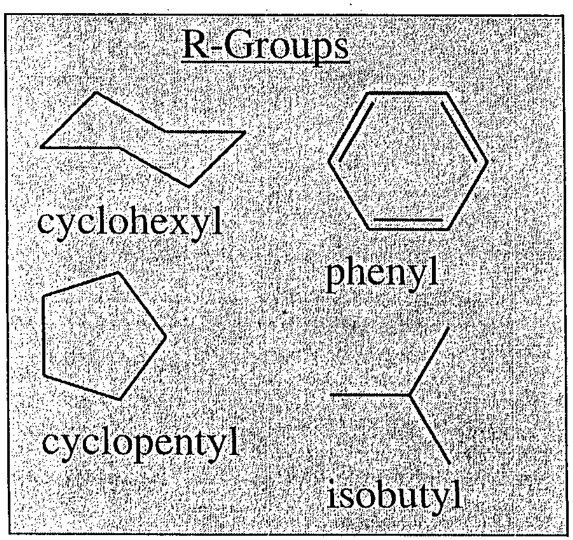
Nonreactive organic (R) groups for solubilization and compatibilization.



May possess one or more functional groups suitable for polymerization or grafting.

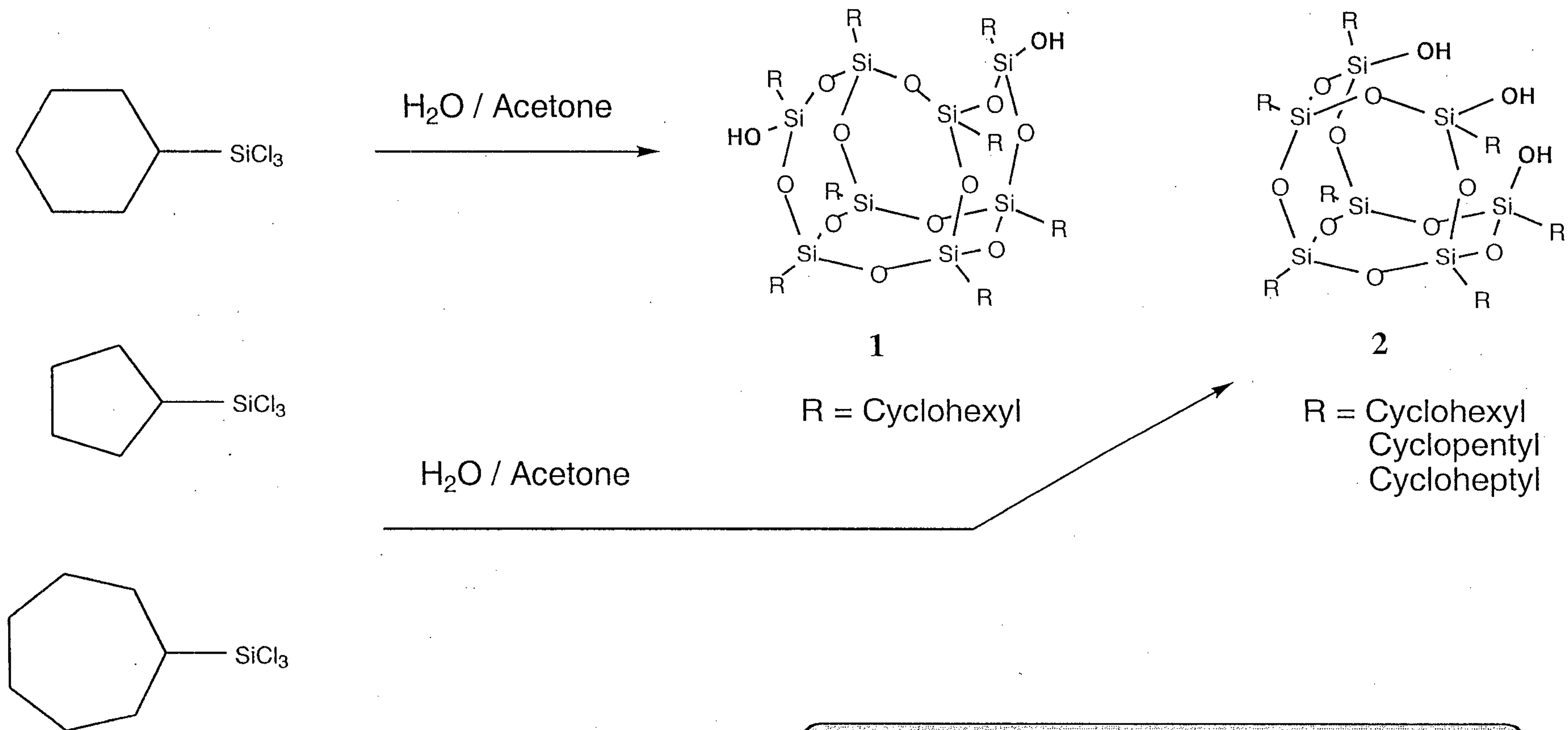
Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.



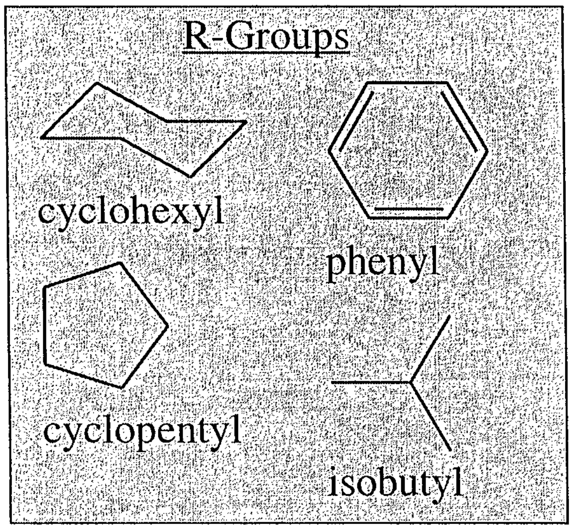
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

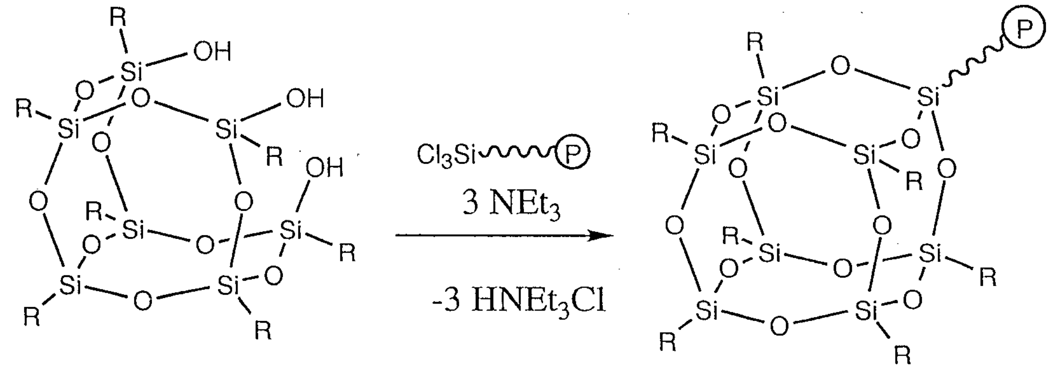
POSS Silanol Synthesis



Brown & Vogt: JACS, 1965, p. 4313
Feher et al: JACS, 1989, p 1741;
Organometallics, 1991, p 2526

POSS Macromers For Nanocomposites





Halides	Nitriles	Silanes	Styryls
Alcohols	Amines	Silanols	α-olefins
Esters	Isocyanates	Silylchlorides	Acrylics
Bisphenols	Epoxides		Norbornenyls

POSS-based macromers are now available through either **Geleste** or **Aldrich**

POSS technology is commercialized by **Hybrid Plastics** in Fountain Valley CA

Why POSS and Why Nano?

1 mm
- Sewing Needle
- Razor Blade Thickness

100 μm
- Human Hair
- Most Cells & Fibers

10 μm

1 μm
- Bacteria, Fillers & Polymer Morphology

100 nm
- Viruses & Nanofillers

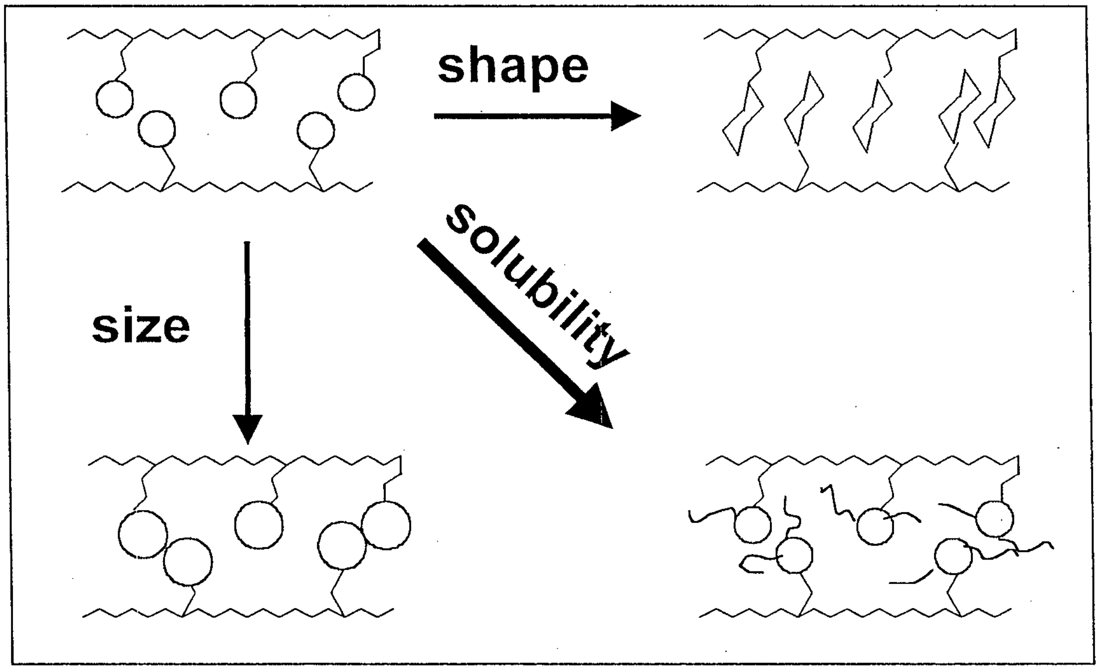
10 nm
- POSS® Building Blocks

1.0 nm
- Macromolecules

0.1 nm
- Atoms / Small Molecules

Field	Property	Critical Length
Electronics	Tunneling	1-100 nm
Optical	Quantum Well	1-100 nm
	Wave Decay	10-1000 nm
Polymers	Primary Structure	0.1-10 nm
	Secondary Structure	10-1000 nm
Mechanics	Dislocation Interaction	1-1000 nm
	Crack Tip Radius	1-100 nm
	Entanglement Rad.	10-50 nm
Therm-Mech.	Chain Motion	0.5-50 nm
Nucleation	Defect	0.1-10 nm
	Critical Nucleus Size	1-10 nm
	Surface Corrugation	1-10 nm
Catalysis	Surface Topology	1-10 nm
Biology	Cell Walls	1-100 nm
Membranes	Porosity Control	0.1-5 nm

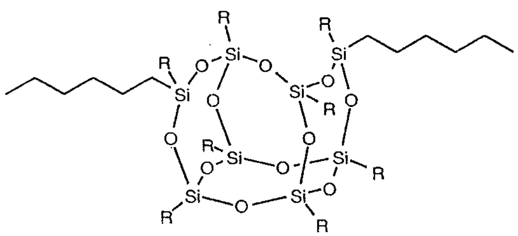
Structure-Property Relationships



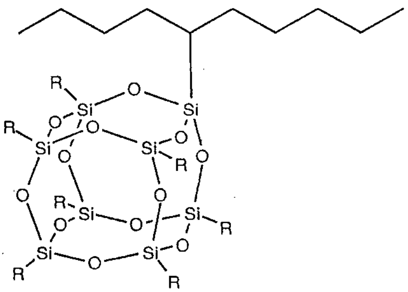
[redacted]

- Maximizing property enhancements through changes at the nano level
- Polymer miscibility vs. POSS/POSS interactions

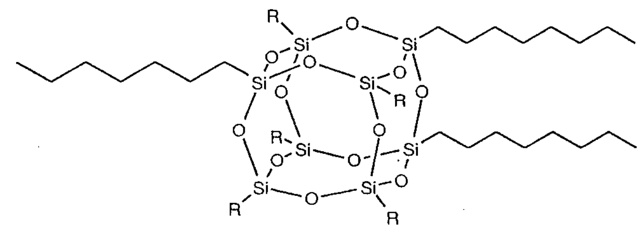
POSS Polymer Incorporation



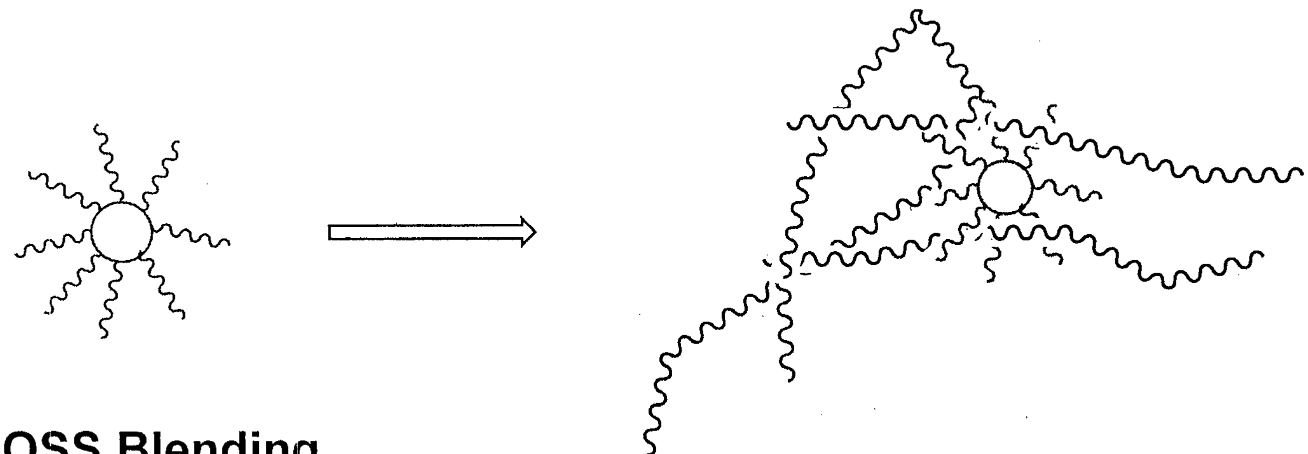
POSS Bead



POSS Pendent



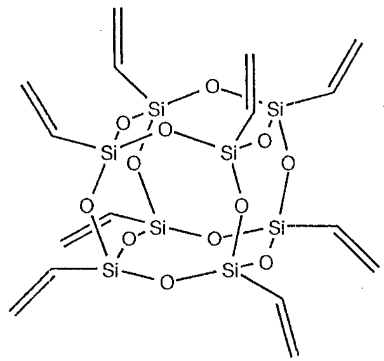
POSS Crosslinking



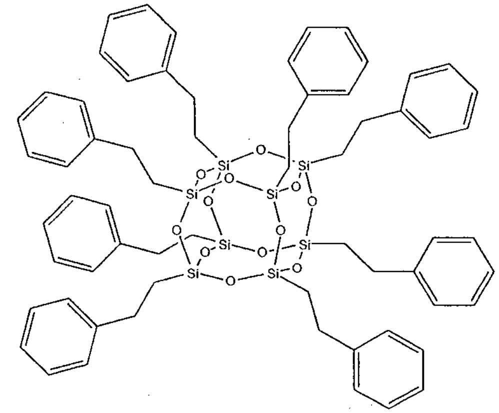
POSS Blending

Size & Shape

50 Wt % POSS Blends in 2 Million MW Polystyrene

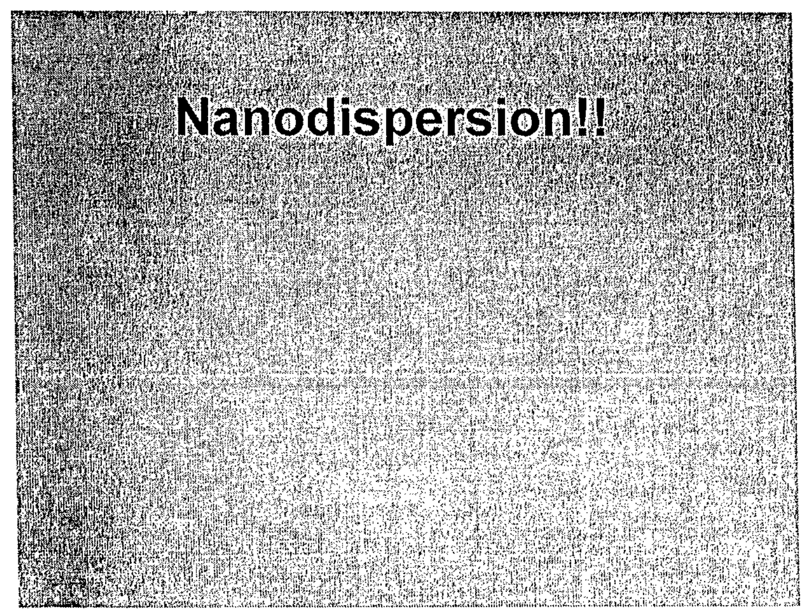


Vi_8T_8

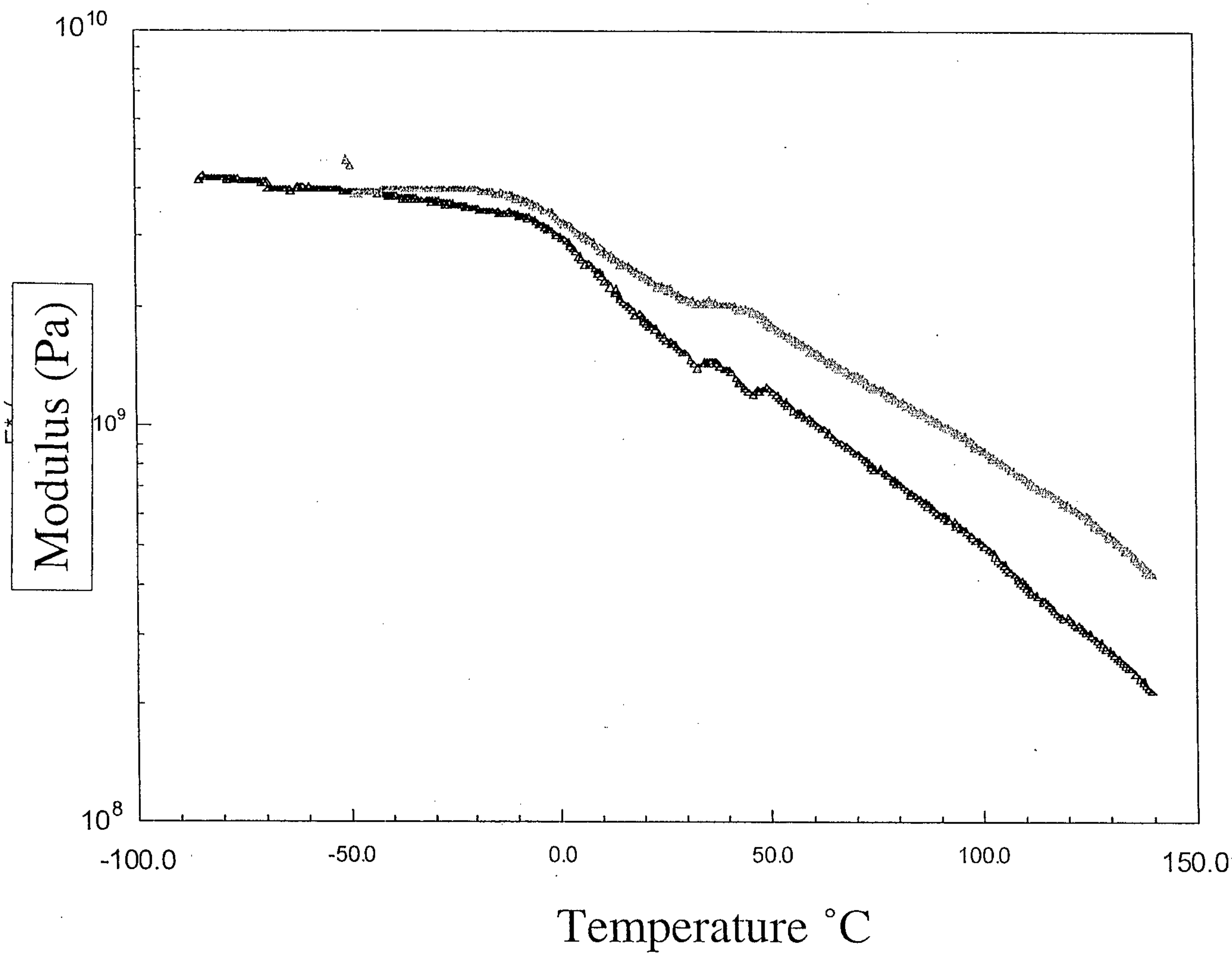


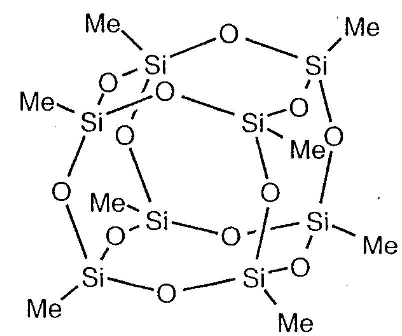
$Phenethyl_8T_8$

1 μm



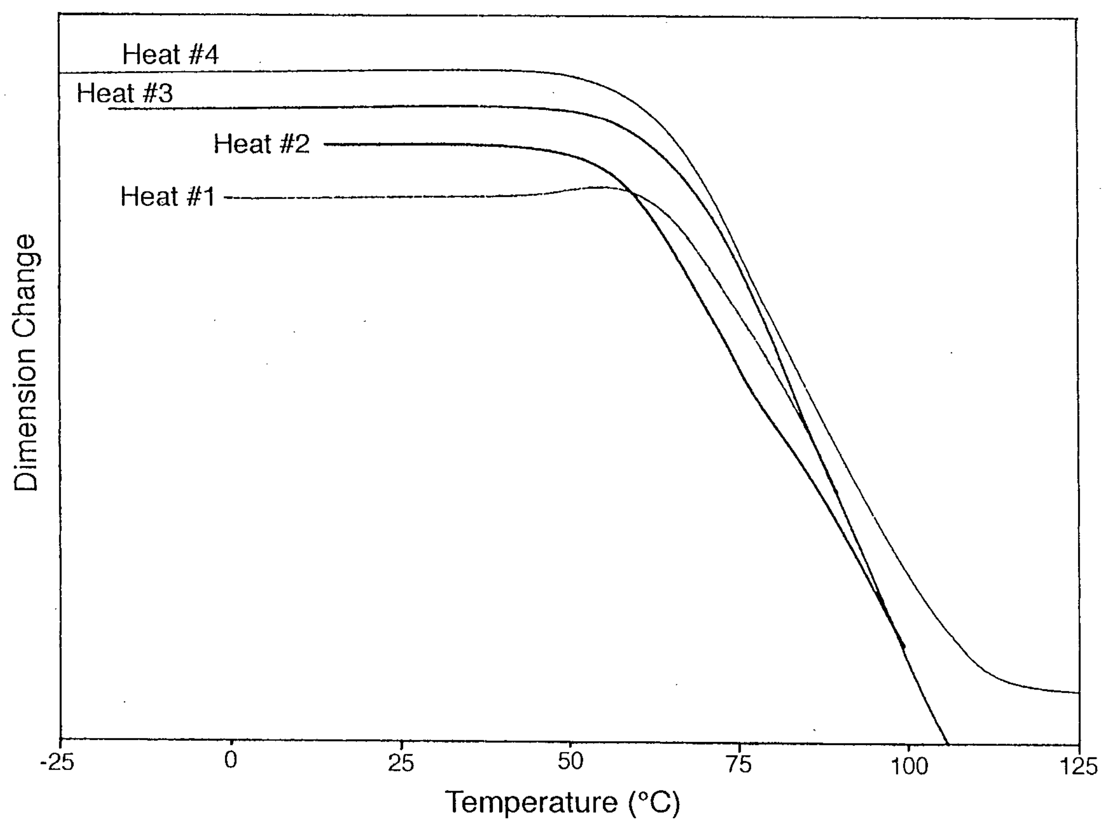
DMA of 10 Wt % POSS in isotactic Polypropylene

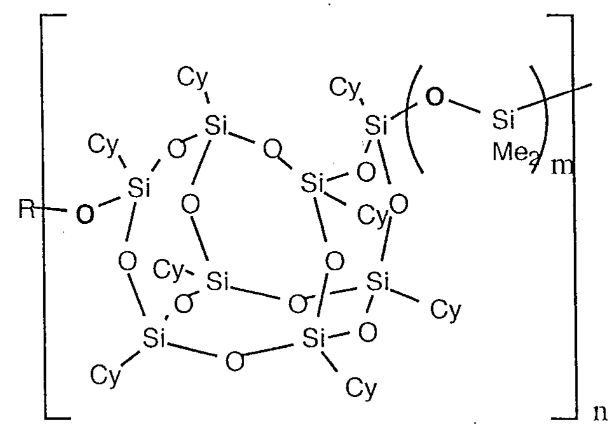




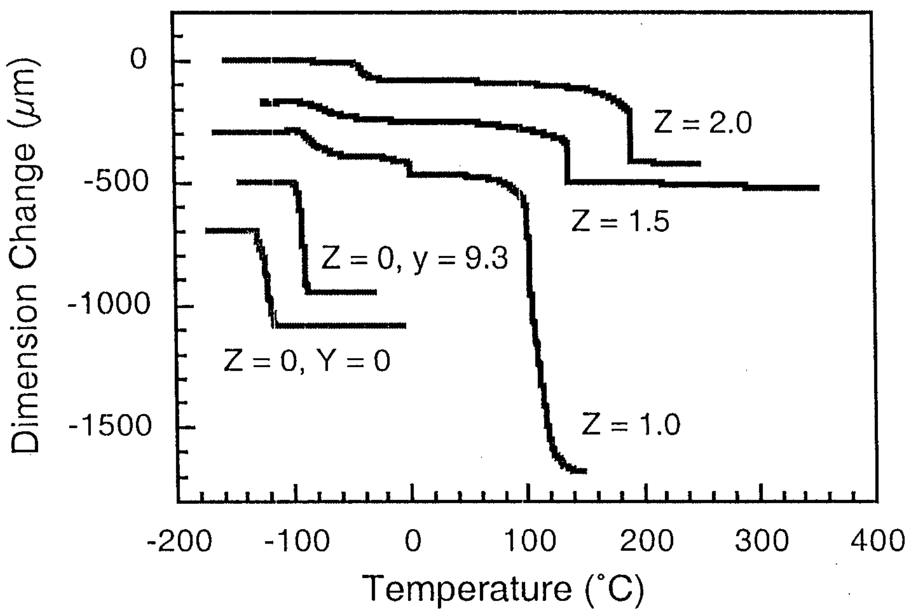
PDMS-POSS TMA Characterization

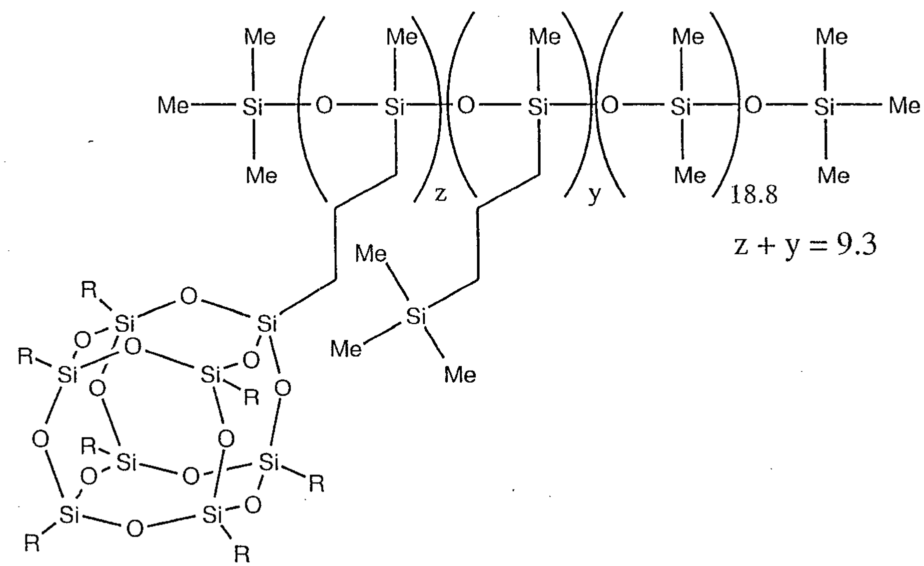
The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.



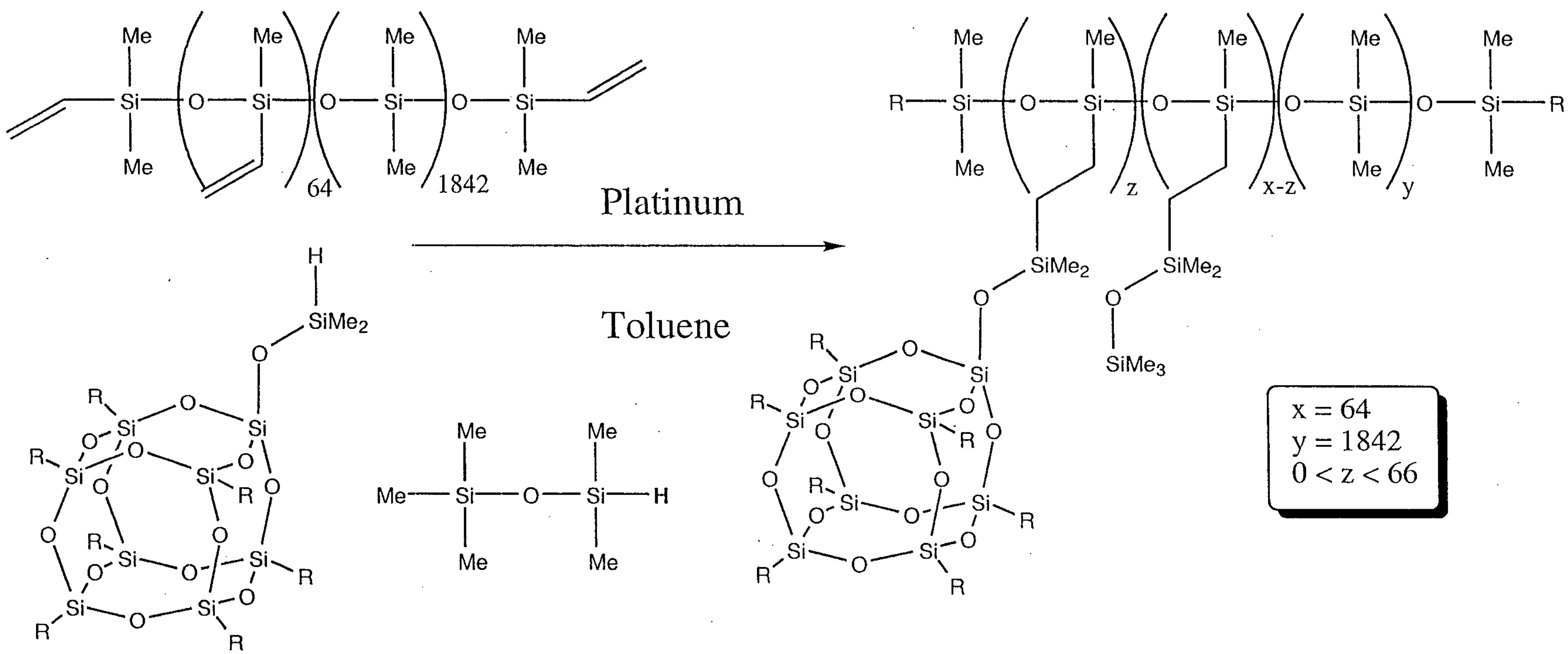


TMA of Pendent POSS-Siloxanes





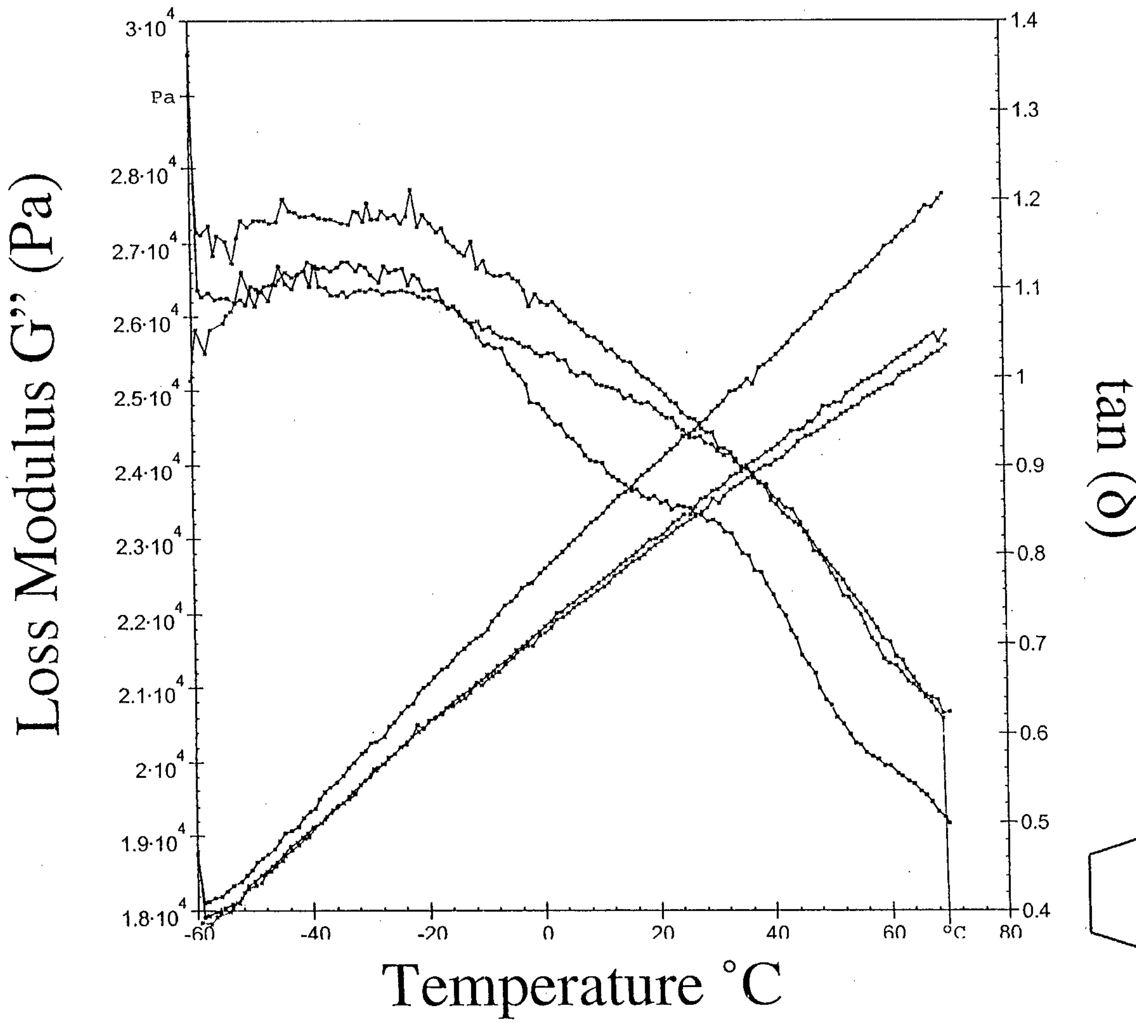
Hydrosilation to High MW PDMS



Used 5 weight % POSS

There are about 7 POSS-macromers per PDMS chain

Comparison of Three T8-POSS Macromers

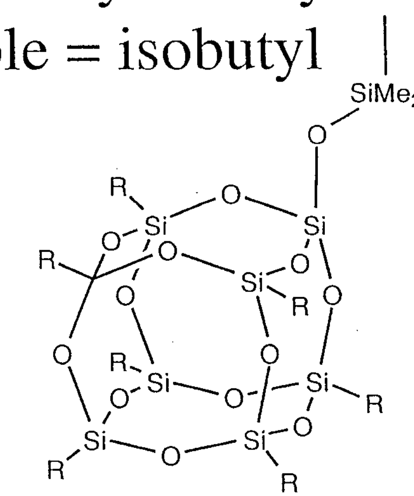


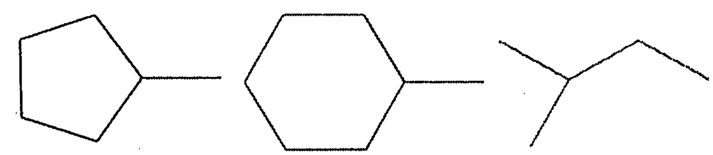
PDMS + 5 wt % POSS

Blue = cyclopentyl

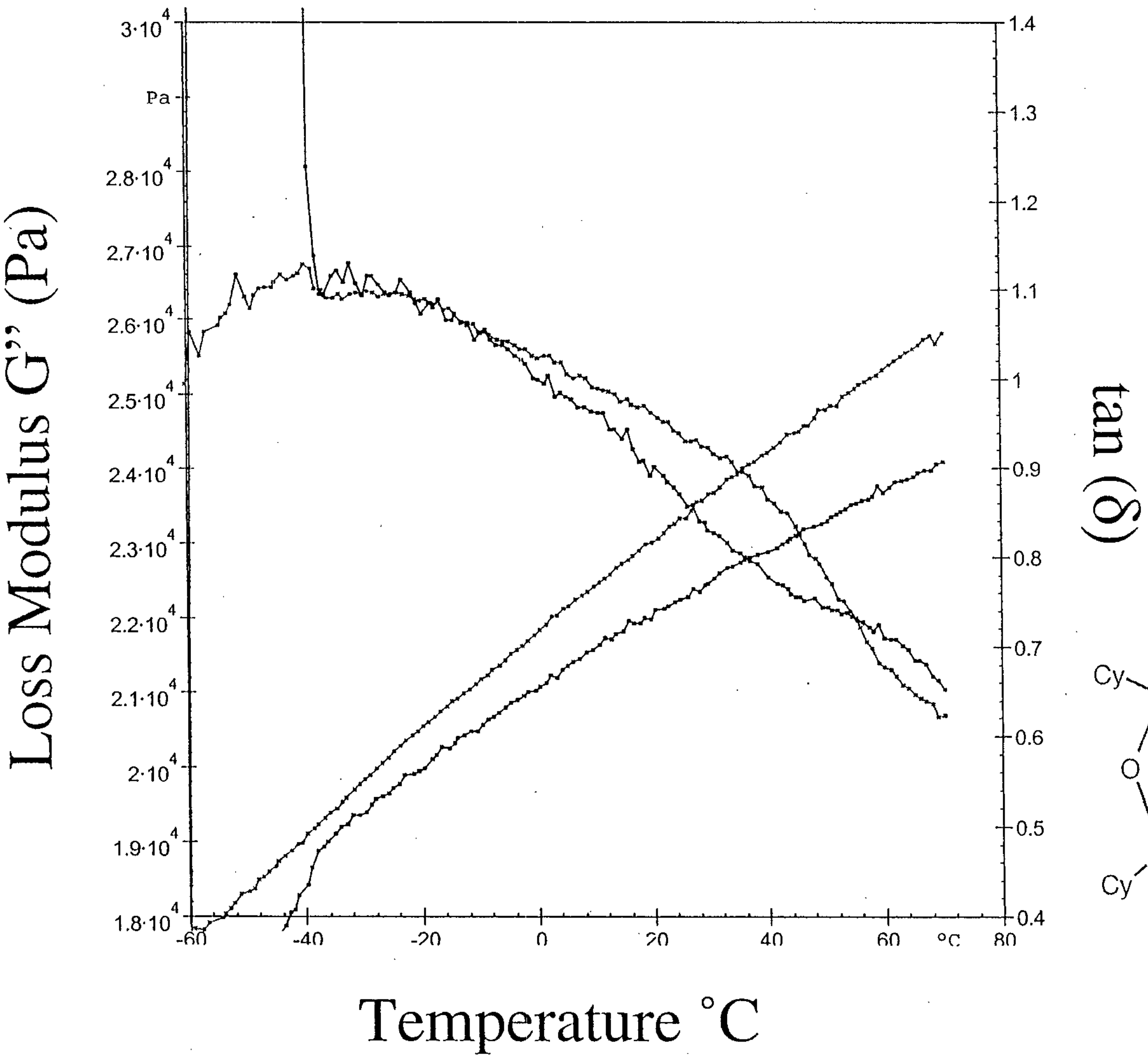
Red = cyclohexyl

Purple = isobutyl





Comparison of Two POSS Polyhedra

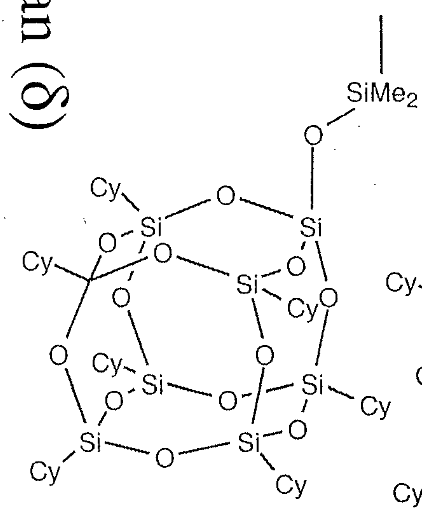


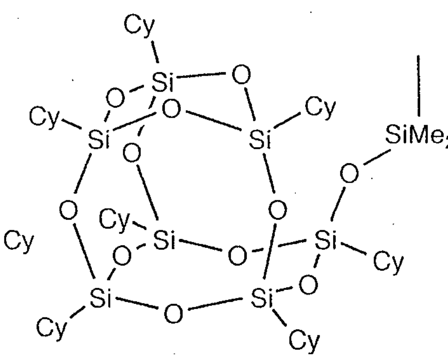
PDMS + 5 wt %

CyclohexylPOSS

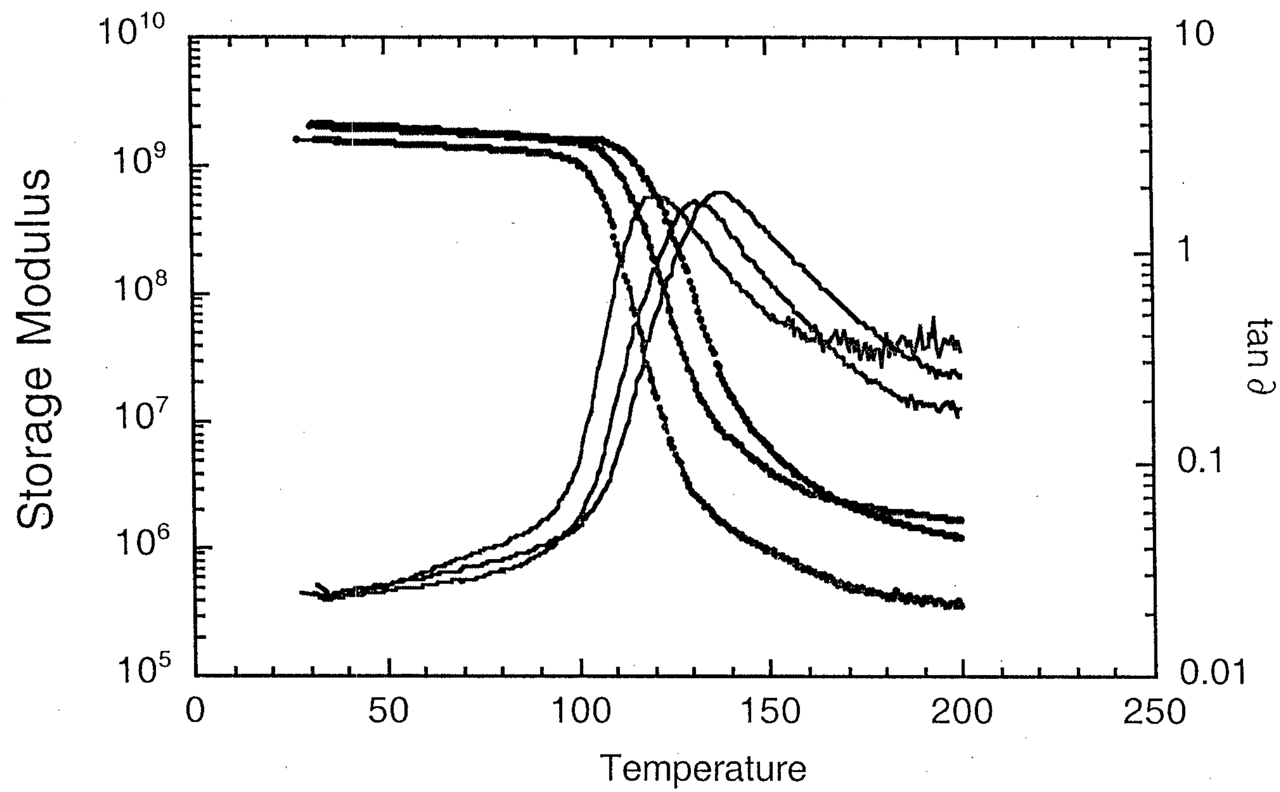
Red = T8-POSS

Blue = T7-POSS



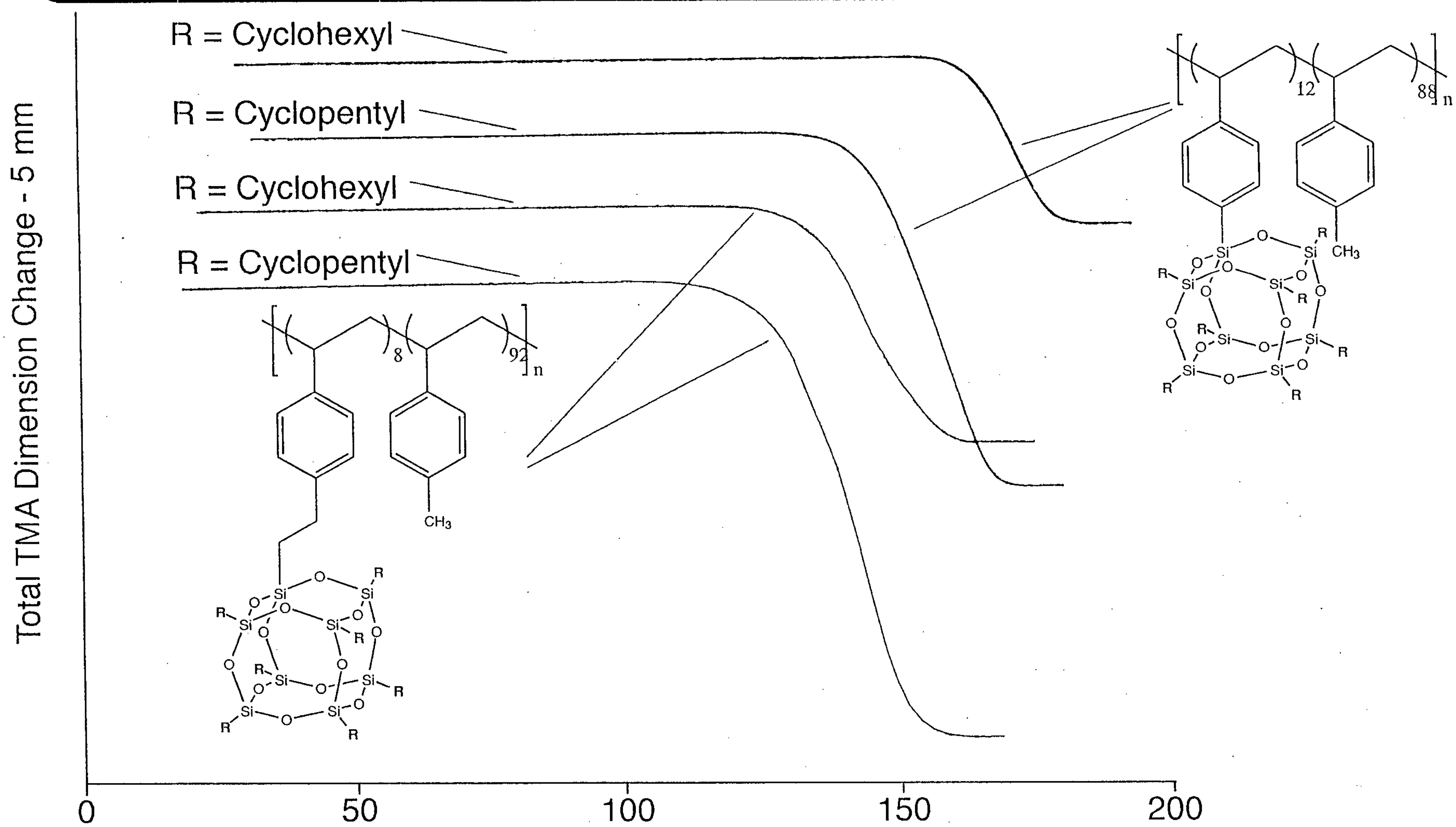


DMA of 30 wt % POSS Polystyrenes

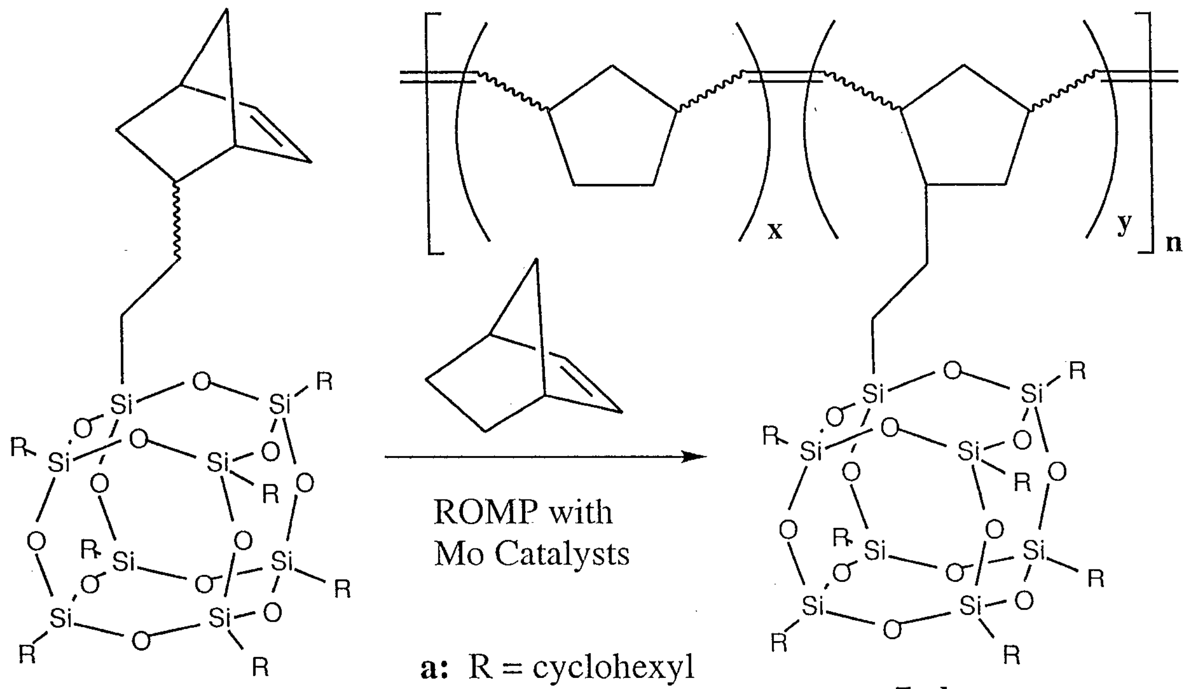


- Comparison of isobutyl, cyclopentyl & cyclohexyl
- Bulk polymerized samples

TMA Plot Comparison For POSS-Styryl and POSS-EthylStyryl Polymers (R = Cyclohexyl and Cyclopentyl)



Polymerization of POSS Norbornenes



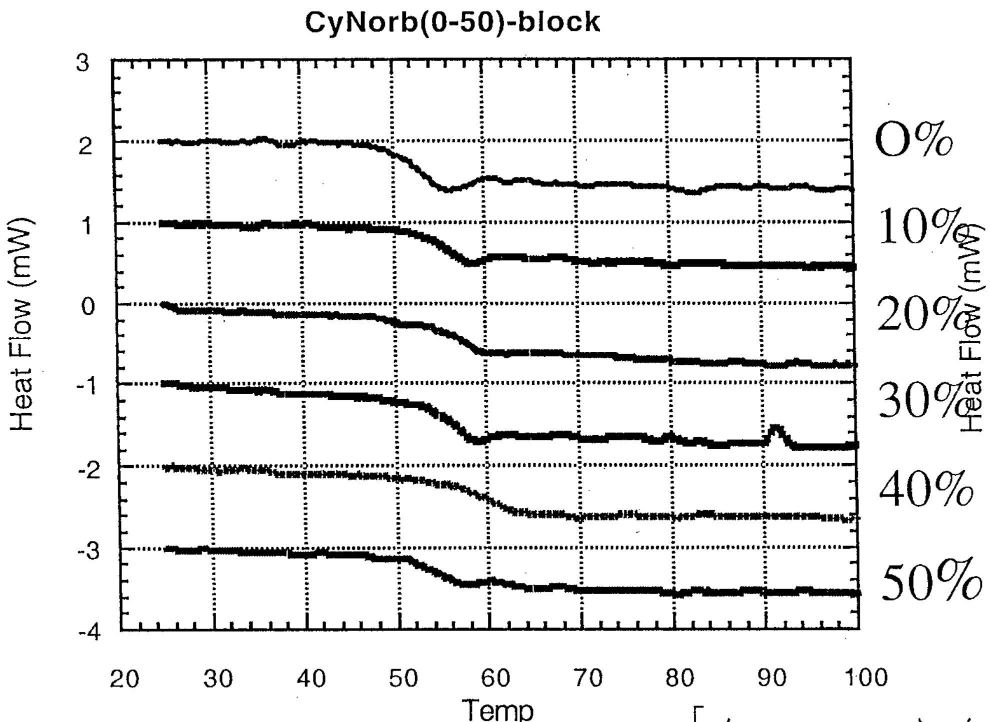
6a,b

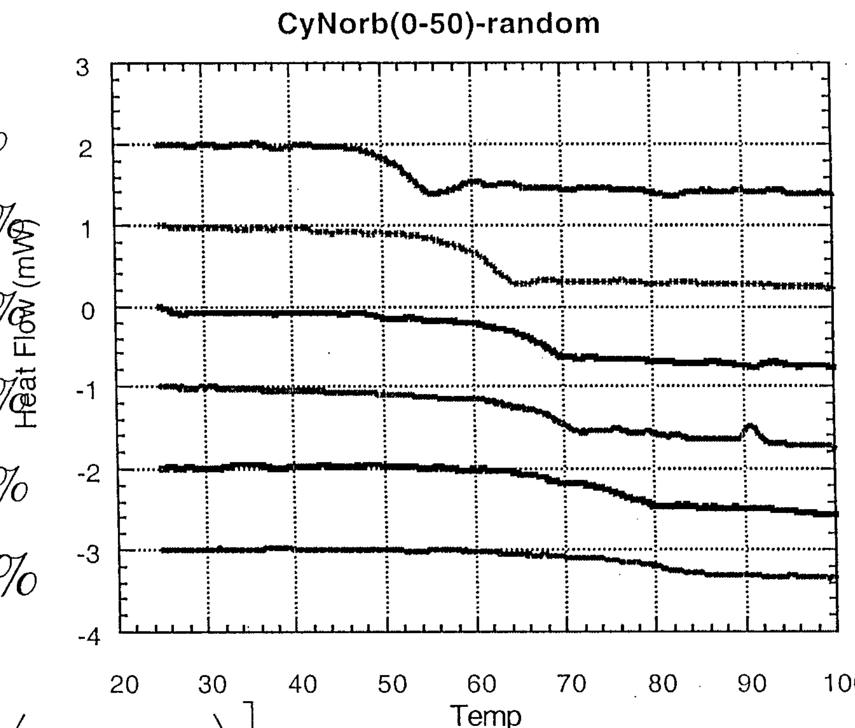
a: R = cyclohexyl
b: R = cyclopentyl

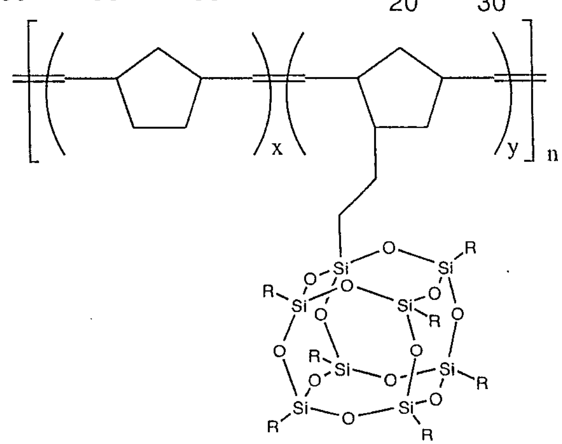
7a,b

Both block and random copolymers were synthesized.
The wt. % POSS was varied from 0 to 50 wt. % POSS.
An ideal polymerization would yield polymers with 500 monomer units.
0 wt % POSS, 0 mole % POSS: x = 500, y = 0
10 wt % POSS, 1 mole % POSS: x = 495, y = 5
50 wt % POSS, 8 mole % POSS: x = 460, y = 40

DSC Data for POSS-Norbornenes

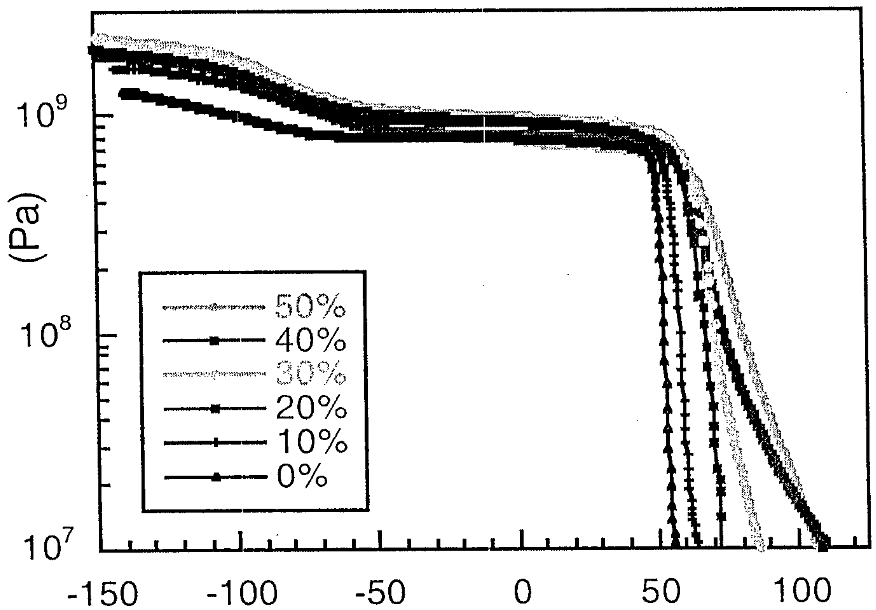


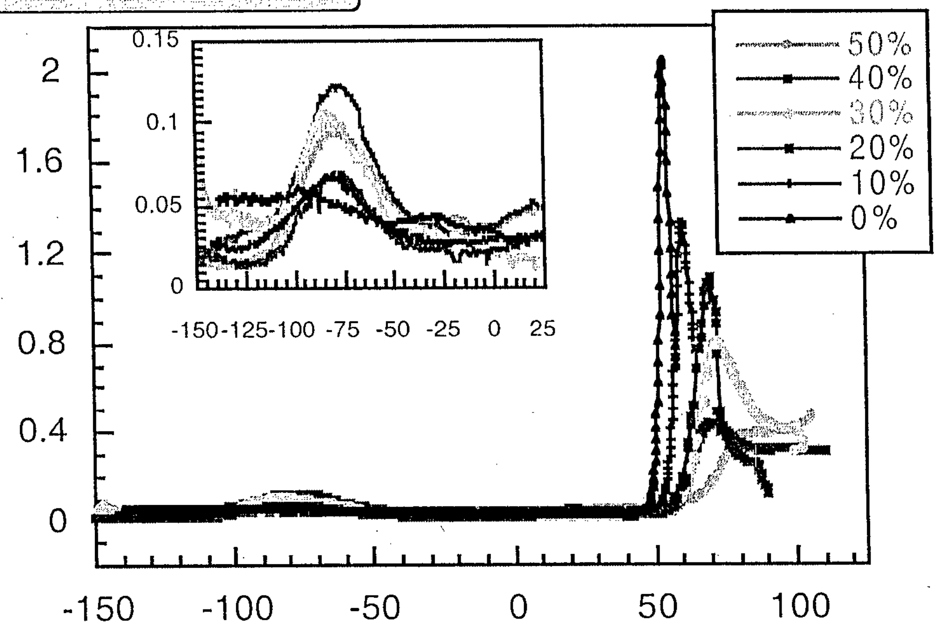


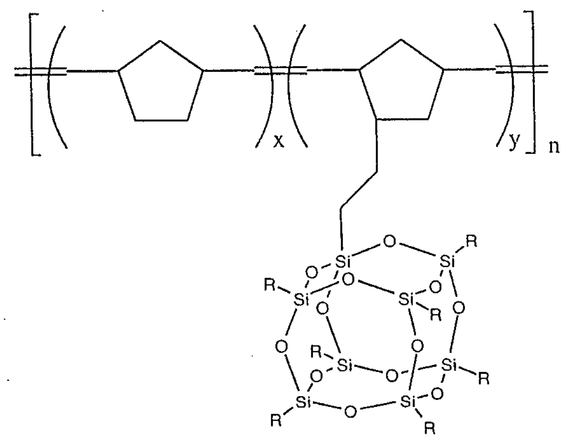


Storage Modulus and Loss Tangent

Cyclohexyl Relaxation: 14.7 kcal/mol





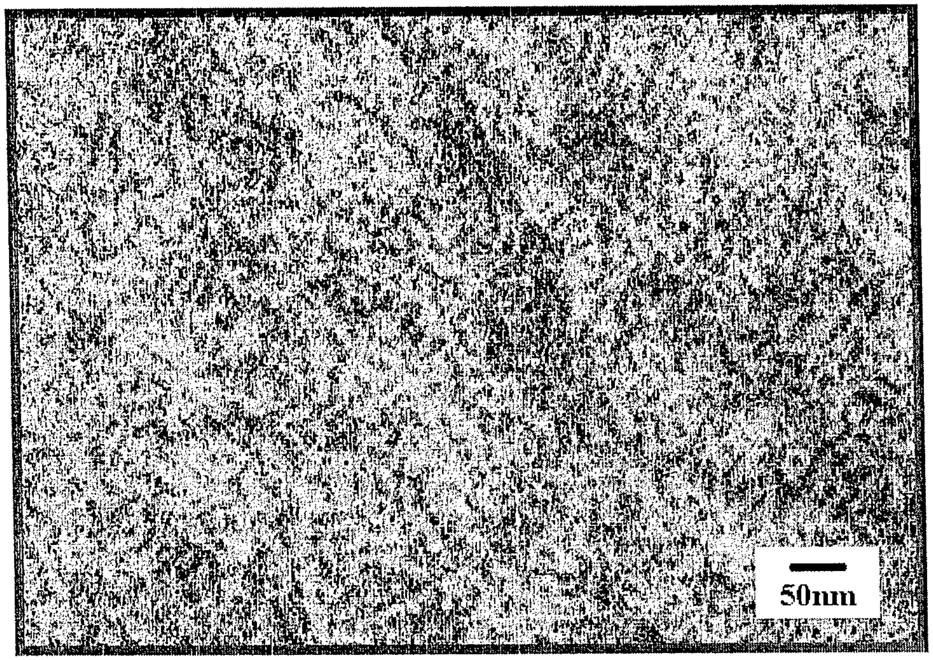


No Maximum for 50% CyPOSS

Various Wt % Cyclohexyl POSS Polynorbornene Random Copolymers

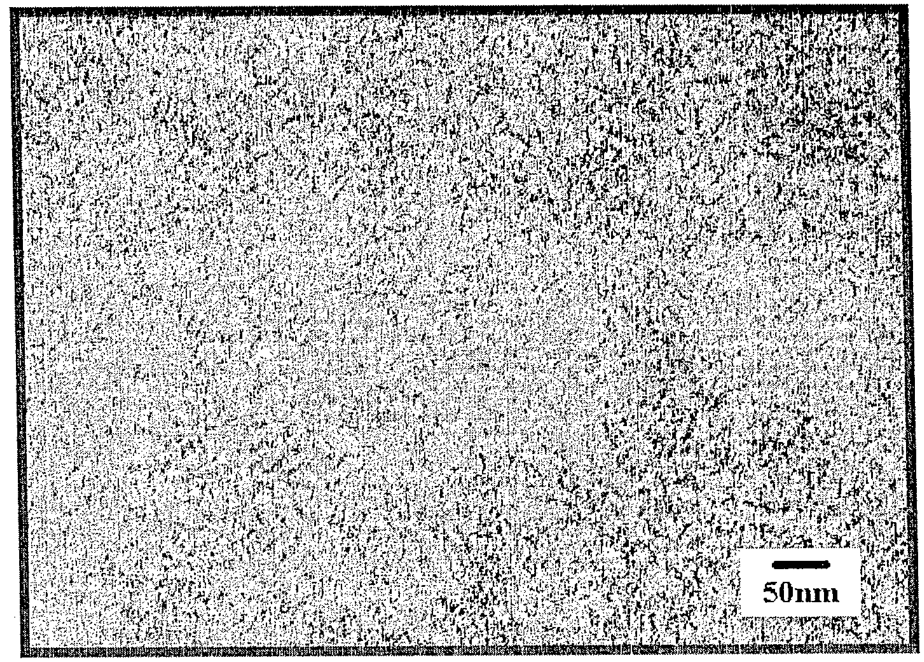
TEM of Random POSS Norbornenes

50CyPOSS/PN



"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

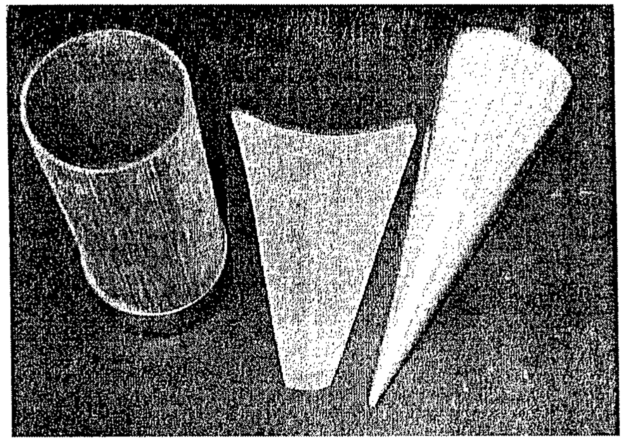
50CpPOSS/PN



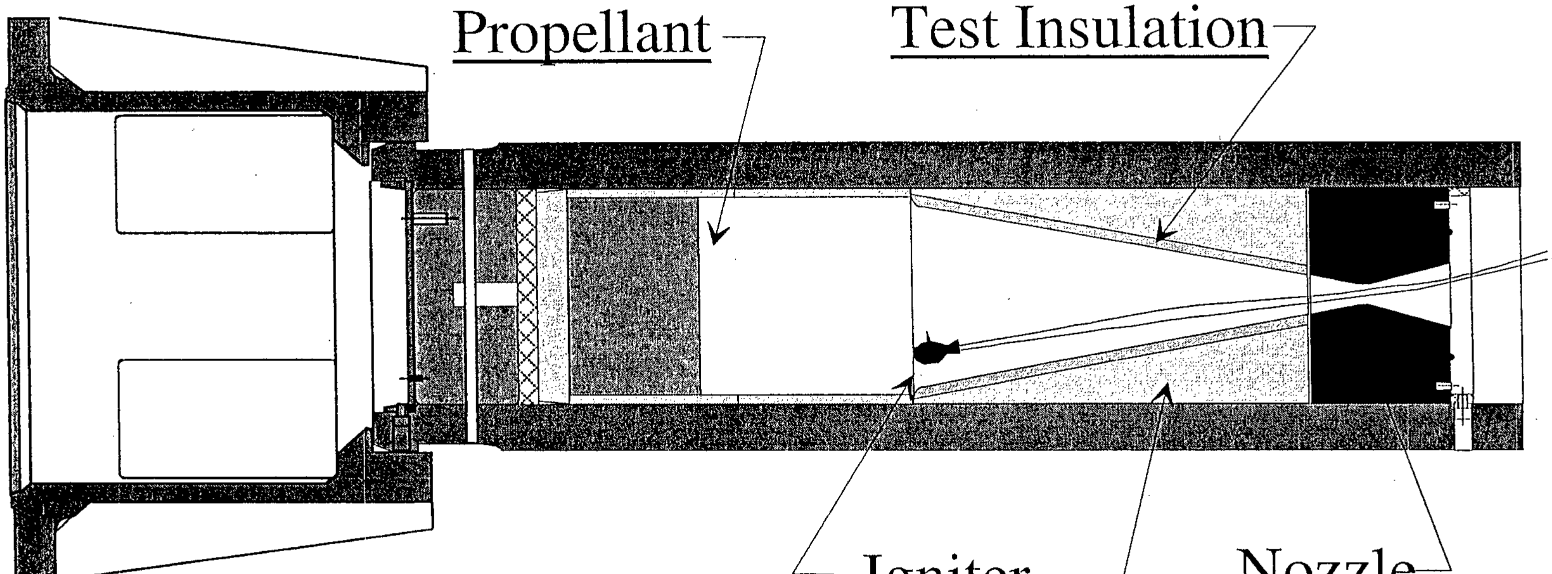
"Fine" Cylinder Nanodstructure
(Diameter ~ 6nm)

CyclohexylPOSS-rich domains may entrain more unoriented polynorbornene chains than CyclopentylPOSS-rich domains.

Solid Rocket Motor Insulation

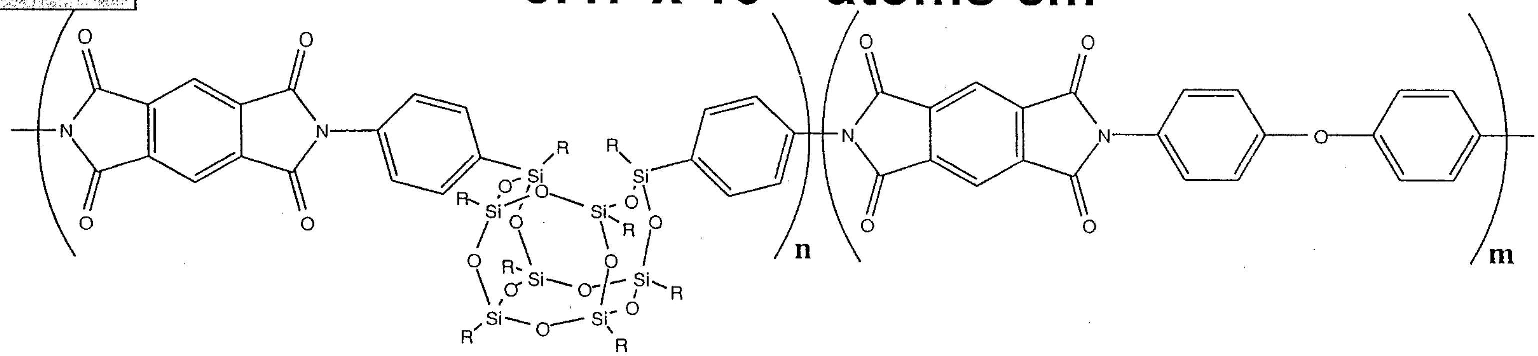


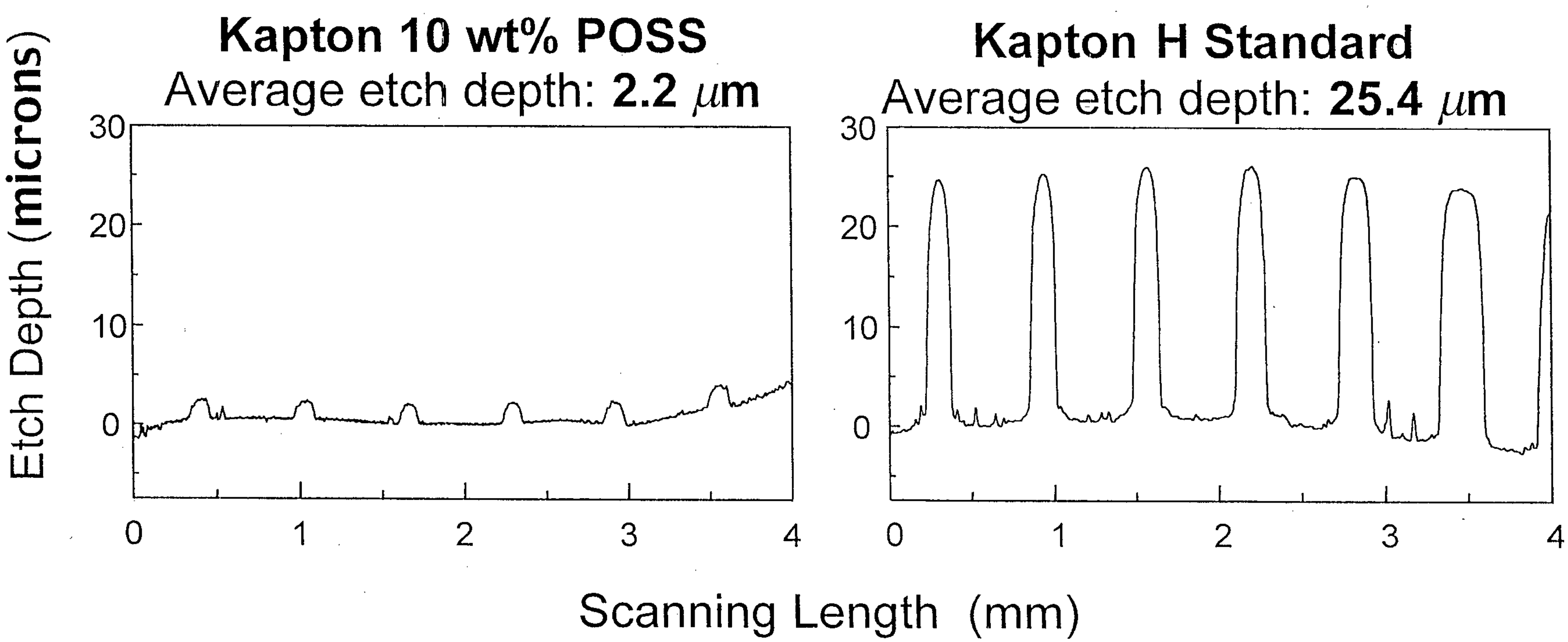
POSS-Insulation Sample



O-Atom Etching Experiment

8.47×10^{20} atoms cm^{-2}





Summary

- The successful incorporation of nano-sized inorganic clusters (POSS) into a wide variety of polymers has been demonstrated.
- These POSS clusters have a remarkable effect on the thermal transitions and mechanical properties of the polymers they are copolymerized into.
- The POSS effect on the properties of analogous polymers shows a dependency on the type of alkyl group on the POSS cluster.
- TEM images of randomly copolymerized polymers illustrate this dependency, as the size of the POSS domains are alkyl-group dependent.
- Rheology of high molecular weight PDMS grafted with small amounts of POSS illustrates a dependence on both the POSS-alkyl-group and POSS shape.

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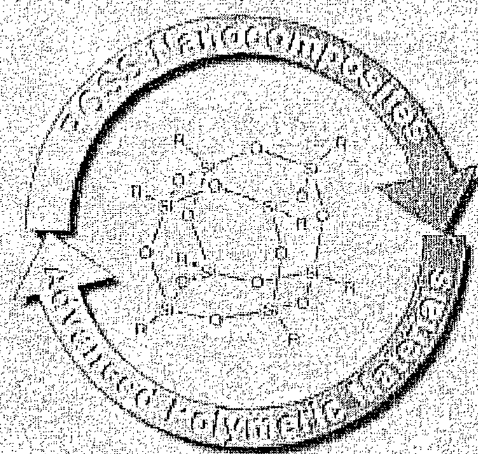
Dr. Shawn Phillips
Dr. Sandra Tomzcak



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Prof. Gar Hoflund UF
Prof. Tim Mitten MSU

Hybrid Plastics Inc.

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